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(21) International Application Number: PCT/US97/06580 (22) International Filing Date: 21 April 1997 (21.04.97) (30) Priority Data: 60/016,478 29 April 1996 (29.04.96) US (71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): GARDNER, Thomas, N. [US/US]; 187 Scenic Drive, Horseheads, NY 14845 (US). MACLEAN, Gregory, K. [US/US]; #4 496 North Hamilton Street, Painted Post, NY 14870 (US). STEMPIN, John, L. [US/US]; 5112 McLaughlin Road, Beaver Dams, NY 14812 (US). WEXELL, Dale, R. [US/US]; 372 West Second Street, Corning, NY 14830 (US). (74) Agent: HERZFELD, Alexander, R.; Corning Incorporated, Patent Dept., SP FR 02-12, Corning, NY 14831 (US).		(81) Designated States: AU, BR, JP, KR, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: ALKALINE BATTERY AND SEPARATOR (57) Abstract <p>A battery (10) having an alkaline electrolyte and a porous, ceramic separator (20), the separator resisting attack by the alkaline electrolyte and having a porous system of sufficient pore size to hold the alkaline electrolyte.</p> <p>The diagram shows a cross-section of the battery (10). It features a positive terminal (+) on the left and a negative terminal (-) on the right. The internal structure includes a positive electrode (14) and a negative electrode (16) separated by a porous ceramic separator (20). The separator (20) is shown with a wavy, porous texture. The battery is filled with an alkaline electrolyte (18). The entire assembly is housed in a container (12).</p>		

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-1-

ALKALINE BATTERY AND SEPARATOR

This application claims the benefit of U.S. Provisional Application No. 60/016,478 filed April 29, 1996, entitled ALKALINE BATTERY AND SEPARATOR, by Thomas N. Gardner, Gregory K. MacLean, John L. Stempin and Dale R. Wexell.

FIELD OF THE INVENTION

The field is alkaline battery construction and a ceramic separator for use therein.

BACKGROUND OF THE INVENTION

Several types of alkaline electrolyte batteries are known in the art. These are commonly categorized on the basis of the characteristic electrodes employed. The different types known include, but are not limited to:

nickel-zinc (Ni/Zn)	aluminum-air (Al/O ₂)
silver-zinc (Ag/Zn)	nickel-metal hydride (Ni/MH)
silver-cadmium (Ag/Cd)	nickel-cadmium (Ni/Cd)
zinc-manganese dioxide (Zn/MnO ₂)	nickel-iron (Ni/Fe)
zinc-air (Zn/O ₂)	

The term "alkaline" refers to the electrolyte being alkaline in nature. This is in contrast to the well-known lead acid battery. The usual alkaline electrolyte is an aqueous solution of KOH which may range from 10% to 45% in strength.

The present invention is generally applicable to all alkaline electrolyte-type batteries. However, development work initially involved the nickel-metal hydride battery. That work led to the nickel-zinc battery. Therefore, the invention is largely described with respect to the latter type of alkaline electrolyte battery.

5 Historically, the nickel-zinc (Ni/Zn) battery resulted from an effort to combine the virtues of the nickel electrode in a nickel-cadmium battery with those of the zinc electrode in a silver-zinc battery. The aim was to achieve the long cycle life time of the nickel-cadmium battery in conjunction with the advantageous high capacity feature of the silver-zinc battery. The Ni/Zn battery concept dates back to work by Drumm et al.
10 in the 1930's.

The Ni/Zn battery has yet to achieve commercial significance, primarily due to the limited cycle life of the zinc electrode. This limits battery life to no more than about 300 cycles of charge/discharge. On repetitive cycling, the zinc electrode partially dissolves in the electrolyte. It redeposits during the cycle, but not necessarily in the
15 same location, or with the same morphology. Consequently, there is a loss of usable active material, capacity decay, and shortened life.

In addition to the material redistribution problem, the redeposited zinc can grow into needle-like dendrites under certain circumstances. These dendrites have a tendency to grow toward the counter electrode and penetrate the separator. This causes short-
20 circuiting of the cells. Efforts have been made to alleviate this problem by additives to the electrolyte, by use of polymeric membrane-type separator materials, and by controlled-charging techniques. However, the problem still persists.

There is a need for an improved porous separator for alkaline electrolyte batteries. A specific need is for a material having a system of pores that inhibit dendrite
25 growth through the separator. The separator material must also function to hold the electrolyte while having a high resistance to chemical attack by that electrolyte. Battery assembly would be facilitated by having available a rigid separator. Such separator could be easily positioned, and would not be subject to movement, or being torn, during assembly or in service.

30 It is a basic purpose of the present invention to provide an improved alkaline electrolyte battery in which these needs are better met. A particular purpose is to

-3-

provide a novel separator for such battery that will remain in place, and thus lessen electrode disintegration and relocation of active material. Another purpose is to provide a separator that will inhibit dendrite growth through the separator.

5

SUMMARY OF THE INVENTION

A battery comprising an alkaline electrolyte and electrodes separated by a porous, ceramic separator, the separator exhibiting good durability when immersed in a KOH solution, and having a porous system of sufficient pore size to hold the alkaline electrolyte.

10

BRIEF DESCRIPTION OF THE DRAWING

The single FIGURE in the accompanying drawing is a side view of a single cell in a Ni/Zn battery.

15

PRIOR ART

Prior literature known to applicants and deemed of possible relevance is listed in a separate document.

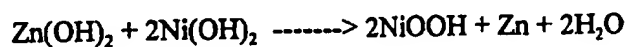
20

DESCRIPTION OF THE INVENTION

The Ni/Zn battery system uses zinc as the negative active material and nickel oxide as the positive active material. The electrolyte is an alkaline KOH solution, normally in the 10% to 45% by weight concentration range. The charge and discharge reactions, in simplified form, are as follows:

25

Charge:



30

Discharge:



The single FIGURE in the drawing is a side view illustrating a single cell 10 of a Ni/Zn battery. Cell 10 is of traditional design consisting of parallel plate, prismatic construction.

Cell 10 embodies a zinc electrode 12. Electrode 12 is a strip of active material composed of a mixture of zinc oxide, additives and binder. It is applied to an electrically conductive substrate 16. The strip may be formed by such known means as electrochemically or chemically precipitating, extruding, or pasting the active material mixture onto conductive substrate 16.

Cell 10 further includes a nickel electrode 14. Electrode 14 may also be in the form of a strip of active material. The strip is composed of a mixture of nickel hydroxide hydrate, additives and binder on an electrically conductive substrate 18. This strip may be formed by such means as electrochemically or chemically precipitating, pasting, or extruding the active material onto the conductive substrate 18.

The conductive substrates serve as current collectors for the electrodes. The nickel strip conductive substrate 18 may be connected to a common positive terminal in single cells. The zinc strip conductive substrate 16 may be connected to a common negative terminal in single cells.

Electrode construction for other alkaline electrolyte battery systems will, likewise, be carried out in accordance with known practice. No novel features with respect to the electrode materials are introduced by the present invention. Accordingly, reference is made to published art for electrode construction details for such other battery types.

Electrodes 12 and 14 are separated by a porous, ceramic separator 20. Separator 20 has the multiple function of providing an electrolyte reservoir for the respective electrodes, retarding zinc, or silver dendrite short-circuiting, and retarding zinc relocation. This is usually accomplished, albeit imperfectly, in existing batteries by using multiple layers of absorbent material, and microporous, or membrane-type, material on the surface of the positive and negative electrodes to retard zinc dendrite penetration. Typical, commercially-available separator materials for Ni/Zn cells are

microporous, polymer membranes composed of such materials as nylon, polypropylene, polyethylene and cellophane.

It is a feature of the present invention that separator 20 is a thin plate of porous, ceramic material. It is a primary purpose of the separator to hold the electrolyte. To
5 this end, there must be sufficient porosity for the purpose, but the pores must not be so large that the electrolyte flows out. Also, the ceramic selected must resist attack by the alkaline electrolyte. In those batteries employing zinc, or silver electrodes, the pore size of the material must be sufficiently small, and the nature of the pores must be highly tortuous, so that dendrite growth through the separator is substantially hindered.

10 We have found that extruded, pressed, or tape cast strips of alumina, mullite, and mixtures thereof, after sintering, meet the several requirements of a ceramic separator for an alkaline electrolyte battery. The material selected is preferably free of uncombined silica which is readily dissolved by an alkaline electrolyte. However, up to one % free silica can be tolerated without undue interference with pore size and stability.

15 The material must, of course, be resistant to appreciable attack by the alkaline electrolyte. We employ a rather severe accelerated test in screening materials. In this test, a piece of the material is immersed for 48 hours in a 30% KOH solution held at 70°C. The test piece is weighed before and after immersion and must show a weight change less than 2% to be accepted.

20 These materials may be extruded, pressed, or cast as thin strips, flat plates, tubes, honeycombs, or channeled structures. The materials, after sintering, have a porosity of about 20-40%. This permits holding adequate alkaline electrolyte, such as KOH solution, to provide the necessary ionic transfer for the charge-discharge cycle. The pore size of these materials is sufficiently small, and the pores thus provided are
25 sufficiently tortuous in nature, to substantially prevent growth of zinc dendrites into and through the separator during operation of a battery with zinc electrodes. This prolongs battery life by inhibiting the loss of active material from the zinc electrode, and by avoiding short-circuiting.

The porosity of a material involves pore volume and pore size. Pore volume
30 represents the percent of the total volume of a body that is constituted by pores. A pore

volume of at least 20-25% is necessary to accommodate the electrolyte in a Ni/Zn battery, and to permit electrical transfer during cycling.

Extruded ceramic materials may provide up to about 40% inherent porosity when fired. Where greater porosity is desired, a combustible additive, such as powdered carbon, or other carbonaceous material, may be included in the batch. When this batch
5 is fired and sintered, the combustible additive is partially or completely removed to leave openings or pores in the ceramic body. While porosities as high as 80% may thus be obtained, we prefer a range of 40-70%.

Pore size has an impact on pore volume. More important, however, is the
10 control that it exercises on material transfer and dendrite growth during cycling. The separator for a battery with a zinc, or silver electrode should have a pore size less than 0.1 micron in diameter, preferably less than 0.05 micron. However, it should be greater than about 0.005 micron in order to provide adequate electrolyte containment and ion mobility in the body.

15 The nickel-metal hydride, nickel-iron and nickel-cadmium batteries do not have as severe a dendrite growth problem as batteries with zinc or silver electrodes. However, they may benefit from other features of a rigid, ceramic separator, such as improved electrode compression and reduced shedding of active materials. For these batteries, a larger pore size in the separator is preferred to provide a greater capacity for
20 electrolyte accommodation and lower resistance to ion flow. The pore size may be greater than 0.1 micron and range up to 20 microns in diameter.

Pore size may be controlled primarily by controlling particle size of batch materials, that is, the ceramic and additives in the extruded or rolled batch. In general, larger particle size batch materials contribute to larger pore size and greater porosity.
25 The mechanical strength of the body, however, tends to be lower so that the body is more fragile. For smaller pore size, fine, presintered batch materials that pack closely may be used.

Pore size in the finished ceramic separator can also be controlled, or reduced, by applying a wash coat to the pores in the original ceramic body. The wash coat applied
30 may be a slurry of either similar, or different, material. Its application is followed by a

-7-

further firing of the body. This wash coating-firing sequence may be repeated, if necessary, until a desired pore size is obtained.

The tape cast process was used to fabricate thin battery separators < 0.25 mm (0.010") in thickness for alkaline battery systems. The tape casting process incorporates a mixture of inorganic materials with binders, solvents, and plasticizers to produce thin, flexible, plastic-like sheets. These thin sheets can easily be cut, punched, or drilled to produce thin, consolidated materials with or without intricate patterns.

Alumina and mullite-alumina ceramic materials, having no free silica, were processed. A typical batch of powdered materials consists of, in parts by weight:

10	Platelet clay	16.66
	Stacked clay	5.54
	Calcined clay	27.6
	Alumina	50.7

The batch was originally formulated for another product where it was necessary to control expansion effects by crystal orientation. Accordingly, a combination of clays was used; a practice that may be unnecessary for present purposes.

Tape casting batches were made in small amounts by mixing the following materials in 500 ml plastic bottles,

	81 g	small ceramic ballmill balls
20	12 g	ethanol
	4 g	polyvinylbutyral
	16.1 g	methylisobutylketone
	0.91 g	Tergitol®
	1.7 g	dibutylphthalate
25	50 g	powdered batch

The tape cast materials were mixed thoroughly after each addition and then roll mixed for 16 hours. After mixing, the samples were cast on a standard tape casting table, using a doctor blade, and allowed to air dry. The thin flexible samples were then cut to size and slowly fired at 1400-1550°C. Porosity and pore size were controlled by the particle size of the batch materials and the firing temperature of the ceramics. Thus, a batch comminuted to an average particle size of 1-10 microns provided a pore size of

0.3-0.4 microns. Thickness of the ceramics ranged from 0.075-0.25 mm (0.003-0.010"). It was controlled by the thickness of the doctor blade and the shrinkage of the ceramics.

5 The same powdered batch materials, with the addition of a binder system including methyl cellulose, a dispersant and water, were used to prepare extruded ceramic separators. The extruded samples were also fired from 1400-1550°C. Porosity and pore size of the extruded ceramics were also controlled by the particle size of the batch materials and the firing temperature of the ceramics. Thickness of the fired ceramics ranged from 0.150-0.550 mm (0.006-0.022"). The initial ceramics used for
10 nickel-metal hydride batteries ranged from 40-60% in porosity. They exhibited a pore size range of 1-2 microns.

The invention is further illustrated with reference to the following specific embodiments:

15

Examples 1-3

A nickel-metal hydride button cell battery made with an alumina separator having 50% porosity was successfully cycled 140 times. The performance of the battery remained constant throughout. By comparison, a control battery made with a non-
20 woven, nylon separator exhibited a small loss in capacity during the same cycle testing. A third battery was made with a 60% porosity alumina separator. This battery demonstrated excellent performance throughout cycling which was stopped after 60 cycles.

25

Examples 4-6

A reduction in the distribution of soluble zinc throughout a cell is significant in reducing the potential for zinc dendrite formation and penetration through a separator. This, in turn, reduces the potential for creating an internal short circuit. Therefore, an
30 experiment was designed to compare the zinc diffusion rates, or flux, through various types of separator materials. This comparison had the potential for indicating how well

a separator may prevent the formation of zinc dendrites. Thus, the higher the zinc diffusion rate, the greater the probability of dendritic shorting occurring.

For test purposes, two solutions of 45% by weight of KOH were prepared. One of the solutions was made 1 molar in ZnO, while the other solution remained free of ZnO. Equal volumes of each solution were placed in a container partitioned by a separator to prevent direct intermingling of the solutions. Three different separators were tested as partitioning members. Diffusion of zinc through each material in a given period of time was measured.

The TABLE below shows the average diffusion rate of zinc through each separator material. Several tests were run with each material, and the average for each material is shown in the TABLE.

		Average Zinc Diffusion Rate
		<u>(moles/cm²/minute)</u>
	<u>Material</u>	
	CELGARD 3400®	1.73×10^{-6}
15	Cellophane	0.47×10^{-6}
	Al ₂ O ₃ sheet (58% porosity)	0.17×10^{-6}

The comparative rates show the superiority of a ceramic separator, in this case alumina, in reducing the diffusion of zinc through a separator, and hence throughout the electrochemical cell.

WE CLAIM:

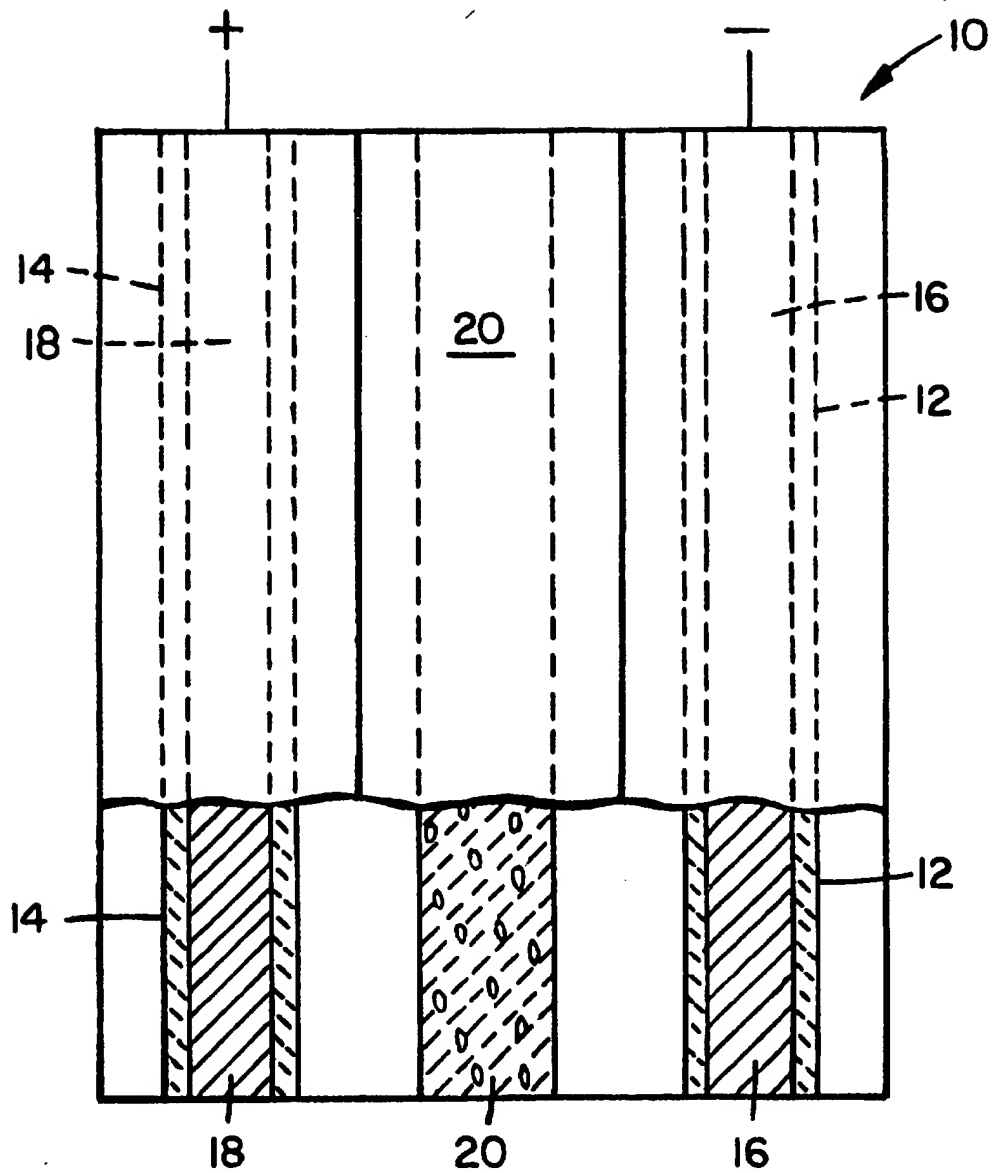
1. A battery comprised of an alkaline electrolyte and electrodes separated by a porous, ceramic separator, the separator exhibiting good durability when immersed in a KOH solution, and having a porous system of sufficient pore size to hold the alkaline electrolyte.
5
2. A battery in accordance with claim 1 wherein the separator is composed of a ceramic selected from the group consisting of alumina, mullite and mixtures thereof, and containing no more than about one % free silica.
10
3. A battery in accordance with claim 2 wherein the selected material is alumina.
4. A battery in accordance with claim 2 wherein the selected material is mullite.
15
5. A battery in accordance with claim 1 wherein the separator has a porosity between 20% and 80%.
6. A battery in accordance with claim 5 wherein the porosity is 40-70%.
20
7. A battery in accordance with claim 1 wherein the electrolyte is a solution of KOH.
8. A battery in accordance with claim 1 wherein the separator form is selected from a group composed of thin strips, flat plates, tubes, honeycombs and channelled structures.
25
9. A battery in accordance with claim 1 wherein the porosity of the separator is enhanced by removal of a carbonaceous material added to the batch from which the separator is produced.
30

10. A battery in accordance with claim 9 wherein the carbonaceous material is a carbon powder.
- 5 11. A battery in accordance with claim 1 having non-zinc, or non-silver electrodes and a ceramic separator having a porous system in which the pores have an average pore size of 0.1-20 microns diameter.
- 10 12. A battery in accordance with claim 1 having a zinc, or silver electrode and a ceramic separator having a porous system with pores of sufficiently small size and sufficiently tortuous nature to inhibit zinc, or silver dendrite growth through the separator.
13. A battery in accordance with claim 12 wherein the pores in the separator are less than 0.1 micron in diameter.
- 15 14. A battery in accordance with claim 13 wherein the pores in the separator have a size in the range of 0.005-0.05 micron.
- 20 15. A porous, ceramic separator for an alkaline electrolyte battery exhibiting a good durability when immersed in a KOH solution, and having a porous system of sufficient pore size to hold the alkaline electrolyte.
- 25 16. A porous, ceramic separator in accordance with claim 15 wherein the separator is composed of a ceramic selected from the group consisting of alumina, mullite and mixtures thereof, and containing no more than about one % free silica.
17. A porous, ceramic separator in accordance with claim 15 that exhibits a weight change of less than 2% when immersed in a 30% KOH solution for 48 hours at 70°C.
- 30 18. A porous, ceramic separator in accordance with claim 16 wherein the selected material is alumina.

19. A porous, ceramic separator in accordance with claim 16 wherein the selected material is mullite.
20. A porous, ceramic separator in accordance with claim 15 wherein the separator
5 has a porosity between 20% and 80%.
21. A porous, ceramic separator in accordance with claim 20 wherein the porosity is 40-70%.
- 10 22. A porous ceramic separator in accordance with claim 15 having a porous system in which the pores have an average pore size of 0.1-20 microns diameter.
23. A porous ceramic separator in accordance with claim 15 having a porous system with pores of sufficiently small size and sufficiently tortuous nature to inhibit zinc, or
15 silver dendrite growth through the separator.
24. A porous, ceramic separator in accordance with claim 23 wherein the pores in the separator are less than 0.1 micron in diameter.
- 20 25. A porous, ceramic separator in accordance with claim 24 wherein the pores in the separator have a size in the range of 0.005-0.05 micron.
26. A porous, ceramic separator in accordance with claim 15 wherein the separator form is selected from a group composed of thin strips, flat plates, tubes, honeycombs
25 and channelled structures.
27. A porous, ceramic separator in accordance with claim 15 wherein the porosity is enhanced by complete or partial removal of a carbonaceous material added to the batch from which the separator is produced.

28. A porous, ceramic separator in accordance with claim 27, wherein the carbonaceous material is a carbon powder.

1 / 1



INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01M 2/16

US CL :429/162, 247

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/162, 247

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN, APS

search terms: separator, ceramic, alkaline electrolyte, alumina, mullite

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,342,709 A (YAHNKE ET AL) 30 August 1994, column 4, lines 9-68, column 6, lines 22-64.	1-28
Y	US 3,861,963 A (AFRANCE ET AL) 21 January 1975, column 3, lines 45-68, column 4, lines 48-68, column 6, lines 23-68, column 7, lines 1-22.	1-28

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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